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# INCREASE IN THE SPECIFIC SURFACE OF HIGHLY POROUS MATERIALS WITH A CELLULAR STRUCTURE

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The process of depositing coatings based on  $\gamma\text{-Al}_2\text{O}_3$  on highly porous ceramic materials with the cellular structure is considered. The deposition was carried out by impregnating samples with boehmite gels produced by hydrothermal treatment of freshly deposited aluminum hydroxide. The possibility of increasing the specific surface of highly porous materials with a cellular structure from 0.1 to 4–9  $\text{m}^2/\text{g}$  is shown.

One of the main tasks of contemporary chemistry and ecology is the development of catalytic processes that take place at high volume rates of gas flows and high dynamic loads. One promising and actively implemented method for solving this problem is the development of processes for deposition of catalysts on highly porous block supports of various structural types that impart sufficient mechanical strength, heat resistance, and high permeability to the catalytic block. The most extensive research in this field is directed to developing supports with a cellular structure which can be used efficiently in neutralization of toxic exhaust of automobiles, industrial enterprises, and power plants and in processes of thorough oxidation and dehydration of hydrocarbons, conversion of methane, etc. [1, 2].

Both cellular materials produced by plastic extrusion and highly porous cellular materials (foam ceramics) produced by the doubling of foam polymers have a rigid three-dimensional structure and impart the necessary physicomechanical and hydrodynamic properties to the catalytic block. However, the use of such materials as catalyst supports is often limited by their relatively small specific surface. Thus, the specific surface of the foam ceramics developed in the Research Institute of Powder Metallurgy (Fig. 1) does not exceed  $0.1 \text{ m}^2/\text{g}$ , whereas the specific surface of catalyst supports for such processes as after-burning of exhaust gases from an internal combustion engine should be at the level of  $5–10 \text{ m}^2/\text{g}$  [3, 4]. In this context, the need arises to deposit a coating with a developed surface (secondary support) on the foam-ceramics structure (primary support), which would make it possible to increase the specific surface of the block by one or two orders of magnitude.

An analysis of the scientific literature [1–5] showed that in most cases researchers use active forms of aluminum oxi-

de, especially  $\gamma\text{-Al}_2\text{O}_3$ , as a universal secondary support. This is determined by the sufficient simplicity of preparing  $\gamma\text{-Al}_2\text{O}_3$  with a specific surface equal to  $100–300 \text{ m}^2/\text{g}$ , its relatively low chemical activity, and the stability of its properties in service at temperatures up to  $700–900^\circ\text{C}$ .

The most common methods for depositing  $\gamma\text{-Al}_2\text{O}_3$  on highly porous primary block supports can be split into three main groups: impregnation of supports with a  $\gamma\text{-Al}_2\text{O}_3$ -based suspension; impregnation of supports with solutions of organic and inorganic compounds that form  $\gamma\text{-Al}_2\text{O}_3$  in decomposition; hydrolysis of soluble aluminum salts accompanied by precipitation of compounds that produce  $\gamma\text{-Al}_2\text{O}_3$  in decomposition (homogenous precipitation) [1–3].

The present work gives results of studying the process of application of  $\gamma\text{-Al}_2\text{O}_3$  on foam ceramics by impregnating it with boehmite gels, subsequent drying, and thermal decomposition of the boehmite. The choice of boehmite as the initial material was determined by the following:

— boehmite gel crystallizes in drying as thin films, which determines the small value of the thermal stresses arising in

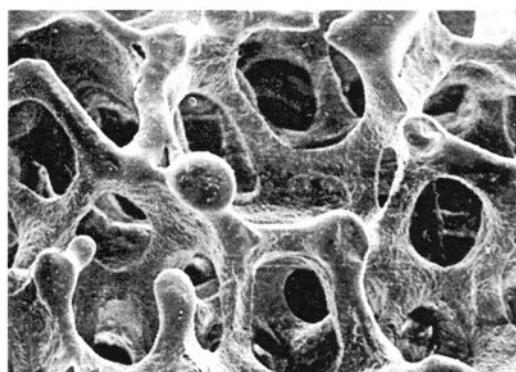


Fig. 1. Structure of foam ceramics.

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heating and decreases the probability of cracking and flaking of the coating in service at high temperatures and in thermocycling;

- the density of boehmite is close to the density of  $\gamma\text{-Al}_2\text{O}_3$ , which reduces the stresses arising in the phase transformations;

- the technology of boehmite gel production is sufficiently simple and well reproducible and can be reduced to hydrothermal treatment of aluminum hydroxide precipitate obtained by chemical condensation from aqueous solutions.

One of the main factors affecting the gel parameters and, consequently, the impregnation process parameters and the specific-surface value is the initial-solution concentration. Thus, it is known that in producing colloidal solutions by chemical condensation, high dispersion of the solid phase and, accordingly, a large specific surface can be achieved by pouring a concentrated solution of one component into a highly diluted solution of the other component under intense stirring. In this case, the rate of seed formation significantly exceeds the rate of crystal growth. On the other hand, under constant values of the pH and the solid-phase concentration, colloidal systems with a smaller size of the particles  $r$  have a higher viscosity (the limiting dynamic shear stress for structurized colloidal systems, to which boehmite gel belongs, is proportional to  $r^{1/2}$ ) [6]. Using gels with increased viscosity can impair the impregnation of porous materials and increase the level of technological waste. Therefore, in selecting the working-solution concentrations, it is necessary to pay special attention to the technological factors, and the purpose of the present study consists not in the development of gels with the maximum possible specific surface, but in the development of a controlled process for making a highly porous cellular material with the needed specific surface ( $5 - 10 \text{ m}^2/\text{g}$ ) that involves the minimum possible levels of technological waste and labor input.

First, the effect of the concentration of the initial components in boehmite gel preparation and the heat-treatment conditions on the specific surface and the phase composition was investigated. Boehmite gels were prepared by hydrothermal treatment (HTT) of aluminum hydroxide obtained by neutralization of an aqueous solution of aluminum nitrate, according to the method described in [7]. To achieve this, under intense mixing  $\text{Al}(\text{NO}_3)_3$  solutions of  $0.2 - 1.5 \text{ M}$  concentration were poured together with a 25% aqueous solution of  $\text{NH}_4\text{OH}$  until reaching  $\text{pH } 9.5 - 10.0$ . Formed precipitates of aluminum hydroxide were washed to  $\text{pH } 7.0 - 7.2$  after a hold, squeezed until the moisture content was  $92 - 93\%$ , and subjected to HTT at a temperature of  $165^\circ\text{C}$  for 4 h.

To determine the dependence of the phase-transformation temperatures on the initial-solution concentrations, the obtained gels previously dried to a constant mass at  $110^\circ\text{C}$  were subjected to differential thermal analysis (DTA). Figure 2 shows a typical derivatogram of decomposition of aluminum hydroxide subjected to HTT (in this case the concentration of the initial solution of  $\text{Al}(\text{NO}_3)_3$  was  $1.0 \text{ M}$ ).

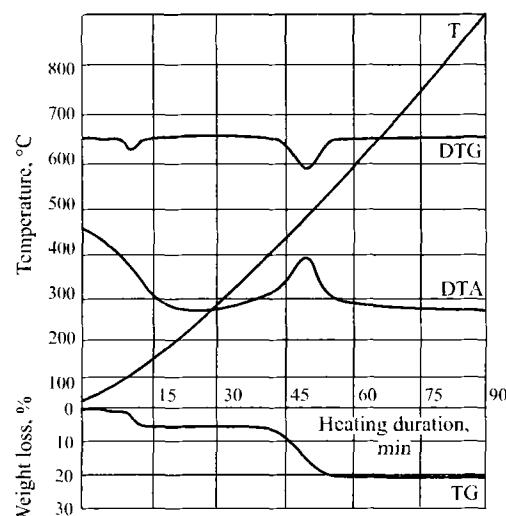


Fig. 2. Derivatogram of boehmite decomposition.

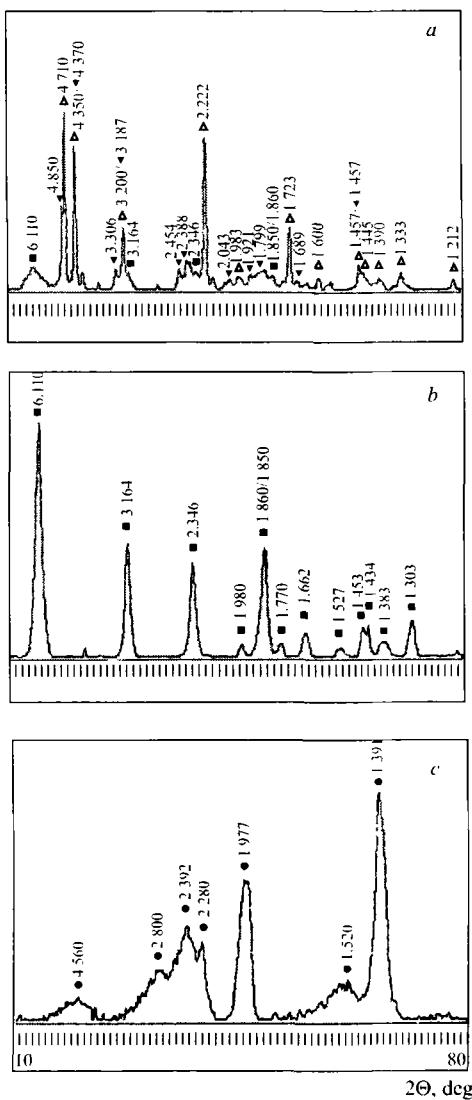
The derivatogram was obtained on a DTA analyzer of the Paulik – Paulik – Erday system in the temperature range of  $20 - 1000^\circ\text{C}$  with the temperature rising at a rate of  $10 \text{ K/min}$ . In all cases, a mass loss of  $4 - 5\%$  was observed in the temperature interval of  $100 - 110^\circ\text{C}$ , related to the removal of adsorbed water. At temperatures of  $450 - 550^\circ\text{C}$ , an exothermic effect with a maximum at  $480 - 500^\circ\text{C}$  accompanied by the loss of mass of  $14 - 16\%$  was observed, which agrees with the calculated mass loss in boehmite decomposition according to the scheme



On the whole, the character of the derivatograms and the temperature effects virtually does not depend on the concentration of  $\text{Al}(\text{NO}_3)_3$ .

Figure 3 presents the x-ray patterns of a precipitate obtained by neutralization of a  $1.0 \text{ M}$  solution of  $\text{Al}(\text{NO}_3)_3$ , the gel resulting from HTT of the precipitate, and the same gel after heat treatment at  $480^\circ\text{C}$ . A phase analysis was carried out on a DRON-3.0 diffractometer in  $\text{CuK}_\alpha$  monochromatized radiation. The phases were identified using the ASTM database.

An analysis of the x-ray patterns showed that the precipitate produced by the reaction of the solutions of  $\text{Al}(\text{NO}_3)_3$  and  $\text{NH}_4\text{OH}$  solutions consisted mostly of two modifications of  $\text{Al}(\text{OH})_3$ , namely, byerite and gibbsite, and a small amount of  $\text{AlOOH}$  represented by boehmite (Fig. 3a). The heterogeneous phase composition of the precipitate was presumably due to the concentration inhomogeneity of the solutions during pouring and mixing. After HTT, a gel with a homogeneous phase composition was formed, whose solid phase was represented by well crystallized boehmite. Heat treatment of boehmite at  $480^\circ\text{C}$  resulted in its decomposition with formation of  $\gamma\text{-Al}_2\text{O}_3$ . The x-ray pattern is blurred, which is often caused by crushing of the crystallites and the appearance of



**Fig. 3.** X-ray patterns of gels obtained by neutralization of  $\text{Al}(\text{NO}_3)_3$ : *a*) after heat treatment at  $160^\circ\text{C}$ ; *b*) after HTT and heat treatment at  $160^\circ\text{C}$ ; *c*) after HTT and heat treatment at  $480^\circ\text{C}$ ;  $\Delta$ )  $\text{Al}(\text{OH})_3$  [byerite];  $\blacktriangledown$ )  $\text{Al}(\text{OH})_3$  [gibbsite];  $\bullet$ )  $\gamma\text{-Al}_2\text{O}_3$ ;  $\blacksquare$ )  $\text{AlOOH}$  [boehmite].

microstresses as a consequence of structural transformations accompanied by changes in the shape and volume of the structural components [8]. An analysis of the crystalline-structure parameters performed using the GOR program, i.e., separation of superimposed lines and precise positioning of lines and line widths, made it possible to identify the formation of a nanocrystalline structure with a size of the region of short-range order of  $20 - 30$  nm. On the whole, the character of the x-ray patterns was virtually identical for all the gels obtained.

Gels synthesized using  $\text{Al}(\text{NO}_3)_3$  solutions of various concentrations were subjected to heat treatment at temperatures of  $160 - 900^\circ\text{C}$ . The purpose was to study the effect of the heat-treatment temperature on the specific surface  $S_m$ ,

**TABLE 1**

Molar concentration of initial $\text{Al}(\text{NO}_3)_3$ , M	Specific surface, $\text{m}^2/\text{g}$ , of $\text{Al}(\text{OH})_3$ precipitate at temperature of $160^\circ\text{C}$	Specific surface, $\text{m}^2/\text{g}$ , of gels obtained by HTT at temperatures, $^\circ\text{C}$				
		160	350	480	700	900
0.2	138	163	167	212	195	161
0.5	120	149	—	204	176	136
1.0	125	146	—	189	151	117
1.5	112	142	—	177	144	101

which was determined on an Acusorb 2100D specific-surface analyzer using low-temperature nitrogen adsorption. The data given in Table 1 show that the largest value of  $S_m$  was achieved by heat treatment of gels at the temperature of the most intense decomposition of  $\gamma\text{-AlOOH}$  ( $480^\circ\text{C}$ ). This is related to pulverization of the crystallites and microcracking caused by microstresses appearing in the structural transformations. As the heat-treatment temperature increases, the microstructure becomes coarser, and  $S_m$  of the resulting aluminum oxide decreases.

Thus, if the cellular support is intended for service at low temperatures, the heat treatment-temperature of the material with the boehmite coating should be around  $500^\circ\text{C}$ . In this case it is possible to ensure complete transformation  $\gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3$ , and  $S_m$  reaches the maximum value. If the cellular support has to serve at temperatures above  $500^\circ\text{C}$ , the heat-treatment temperature ought to be below this temperature. At temperatures above  $700^\circ\text{C}$ , a perceptible decrease in the specific surface of  $\gamma\text{-Al}_2\text{O}_3$  is registered (Table 1), and this imposes certain restrictions on possible application areas of the considered materials.

The second phase of the work was related to studying the process of application of coatings based on  $\gamma\text{-Al}_2\text{O}_3$  on ceramic materials with a cellular structure. Foam-ceramics samples based on mullite with a porosity of  $83 - 85\%$ , a cell size of  $3 - 4$  mm, and a specific surface of  $0.05 - 0.07 \text{ m}^2/\text{g}$  were impregnated with boehmite gels produced using the technology described above. After impregnation, the foam-ceramics samples were centrifuged at an overload of  $25\text{g}$  and dried at a temperature of  $150^\circ\text{C}$ . After that the impregnation operation was repeated. The moisture content of the gels was  $93 \pm 0.2\%$  in all cases. After reaching a mass increase of  $4 - 6\%$ , the samples were heat-treated at  $700^\circ\text{C}$  for 2 h, after which their specific surface was determined.

The resulting gels had different viscosities that increased perceptibly as the concentration of the initial  $\text{Al}(\text{NO}_3)_3$  decreased. On the one hand, this increased the sample mass increment in one impregnation, and on the other hand, it hampered the impregnation process and increased the technological waste. It was impossible to impregnate a sample with gel produced from a  $0.2$  M solution of  $\text{Al}(\text{NO}_3)_3$  unless a vibration load was applied.

**TABLE 2**

Molar concentration of initial $\text{Al}(\text{NO}_3)_3$ , M	Increase in cellular-support mass after boehmite coating application, %			Mass increment after heat treatment at 700°C, %	Specific surface, $\text{m}^2/\text{g}$
	1 impregnation	2 impregnations	3 impregnations		
0.5	3.23	6.13	—	5.22	8.4
	3.29	6.55	—	5.57	9.1
	2.94	5.92	—	5.05	8.2
1.0	1.68	3.61	5.40	4.56	6.7
	1.87	4.10	5.75	4.90	7.0
	1.51	3.79	5.13	4.38	6.3
1.5	1.31	3.03	4.21	3.58	5.0
	1.60	2.80	3.95	3.36	4.3
	1.53	3.01	4.07	3.45	4.5

It can be seen from the data in Table 2 that the most intense mass increment in the samples occurred in using gels obtained from a 0.5 M  $\text{Al}(\text{NO}_3)_3$  solution and amounted to 5.9–6.5% with respect to the initial-sample mass. The amount of deposited  $\gamma\text{-Al}_2\text{O}_3$  determined after calcination of the samples at 700°C was equal to 5.0–5.6%, and the specific surface of the samples increased to 8.2–9.1  $\text{m}^2/\text{g}$ . For gels synthesized using 1.0 M and 1.5 M solutions, the mass increment after three impregnations was 5.1–5.8% and 3.9–4.2%, respectively, which corresponded to the quantities of deposited  $\gamma\text{-Al}_2\text{O}_3$  of 4.4–4.9 and 3.4–3.6%, respectively. The specific surface of the foam-ceramics samples increased to 6.3–7.0 and 4.3–5.0  $\text{m}^2/\text{g}$ , respectively, and 1–2 additional impregnations would have been needed to reach the value of  $S_m$  obtained in the first variant.

Thus, the use of less concentrated working solutions ensures reaching the required specific surface in highly porous materials with a smaller number of technological operations.

However, in using gels obtained from a 0.5 M solution, the technological waste in centrifuging was 85–89%, whereas these losses for the other two types of gel did not exceed 18–20%, which makes the latter technologically more effective.

Boehmite gels obtained by hydrothermal treatment of aluminum hydroxides can be used as initial materials for depositing coatings based on  $\gamma\text{-Al}_2\text{O}_3$  on highly porous cellular materials. The proposed method makes it possible to produce highly porous cellular materials with a specific surface above 5  $\text{m}^2/\text{g}$  that can be used as block catalyst supports. This method allows the control of the process of increasing the specific surface of the material by selecting the number of impregnations and varying the concentration of the initial components used in boehmite gel preparation.

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